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PURANDARE, Y. P. <<http://orcid.org/0000-0002-7544-9027>>, EHIASARIAN, A. P. <<http://orcid.org/0000-0001-6080-3946>> and HOVSEPIAN, P. E. <<http://orcid.org/0000-0002-1047-0407>>

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PURANDARE, Y. P., EHIASARIAN, A. P. and HOVSEPIAN, P. E. (2008). Deposition of nanoscale multilayer CrN/NbN physical vapor deposition coatings by high power impulse magnetron sputtering. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 26 (2), 288-296.

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Deposition of nanoscale multilayer CrN/ NbN PVD coatings by High Power Impulse Magnetron Sputtering

Y.P. Purandare, A.P. Ehiasarian and P. Eh. Hovsepian

NanoTechnology Centre for PVD Research,
Materials and Engineering Research Institute,
Howard Street, Sheffield Hallam University,
Sheffield, S1 1WB
UK.

Abstract

Nanoscale multilayer CrN/NbN PVD coatings are gaining reputation for their high corrosion and wear resistance. However the CrN/NbN films deposited by ABSTM (Arc Bond Sputtering) technology have some limitations such as macro droplets, porosity and less dense structures.

The novel HIPIMS (High Power Impulse Magnetron Sputtering) technique produces macroparticle free, highly ionised metal plasma which brings advantages in both surface pre-treatment and coating deposition stages of the PVD process.

In this study, nanoscale multilayer CrN/NbN PVD coatings were pre-treated and deposited with HIPIMS technology and compared with those deposited by HIPIMS-UBM and by the

ABSTM technique. In all cases Cr⁺ etching was utilised to enhance adhesion by low energy ion implantation. The coatings were deposited at 400° C with substrate biased (U_b) at -75 V. During coating deposition, HIPIMS produced significantly high activation of Nitrogen compared to the UBM as observed with mass spectroscopy.

HIPIMS-deposited coatings revealed a bi-layer period of 4.1 nm (total thickness- 2.9 μm) and hardness of 3025 HK_{0.025}. TEM results revealed droplet free, denser microstructure with (200) preferred orientation for the HIPIMS coating owing to the increased ionisation as compared to the more porous structure with random orientation observed in UBM coating. Dry sliding wear coefficient (K_c) of the coating was $1.8 \times 10^{-15} \text{ m}^3\text{N}^{-1}\text{m}^{-1}$ whereas the steady state coefficient of friction was 0.32.

Potentiodynamic polarisation tests revealed higher E_{corr} values, higher pitting resistance (around potentials + 400 to + 600 mV) and lower corrosion current densities for HIPIMS deposited coatings as compared to the coatings deposited by ABS or HIPIMS-UBM. The corrosion behaviour of the coatings qualitatively improved with the progressive use of HIPIMS from pre-treatment stage to the coating deposition step.

Keywords: Multilayer, nanoscale CrN/NbN PVD coating, HIPIMS, corrosion.

1. Introduction:

Growing concerns of environmental problems have demanded a suitable replacement for the electroplating technology for hard chrome coating due to its toxic waste disposal and hazardous process operating conditions. PVD techniques have proven to be a suitable alternative for the electroplated coatings, which provide a range of thin, hard, wear and corrosion resistant functional coatings. For example nanoscale multilayer CrN/NbN PVD coatings offer an excellent choice in replacing hard chrome and monolithic CrN coatings [1-3]. Nanoscale multilayer CrN/NbN PVD coatings have been successfully deposited by various techniques such as Cathodic Arc Evaporation (CA), Unbalanced Magnetron (UBM) Sputtering and Arc Bond Sputtering (ABS), (combination of CA etching followed by UBM sputtering coating deposition) [3-5]. However coating deposition by these techniques has fundamental limitations; growth defects due to macroparticle formation in processes employing CA technique [4, 6] and under dense structures with intergranular voids for UBM [7]. These growth defects are the weak areas in the coating which not only affect its mechanical properties [8, 9] but also affect its corrosion resistance by facilitating 'solution path' galvanic corrosion [10-12]. Increasing demand for optimised performance has placed a huge emphasis on deposition of defect free coating with dense microstructure.

High Power Impulse Magnetron Sputtering (HIPIMS) technique provides an unique alternative to the conventional techniques. This novel technique facilitates plasmas rich with metal ions (M^+) without a droplet phase and can be used to deposit defect-free dense coatings, in combination with or without substrates biasing [13]. Previous work on the deposition of monolithic CrN coatings by HIPIMS has shown coatings with dense microstructure, low friction coefficient and low sliding wear rate as compared to UBM and

ABS deposited coatings [13]. Also, recent work on the substrate pre-treatment (etching) with Nb^+ ions has shown that HIPIMS can be used to produce coatings with excellent adhesion and corrosion resistance [14]. The improved adhesion is a result of droplet free, clean and crystalline substrate-coating interface due to the incorporation of low energy metal ions into the substrate which promote local epitaxial growth of the coating [15]. However utilisation of the HIPIMS technology for the deposition of nanolayer structures has not been reported.

The present study focuses on extending the understanding of HIPIMS technology from the etching step to the multilayer structured bulk coating deposition step. For the first time, novel **HIPIMS** technology has been utilised to deposit nanoscale multilayer CrN/NbN PVD coatings in an industrial sized PVD coater. Following the deposition, the coatings were characterised and compared to the CrN/NbN coatings deposited by the ABS and the HIPIMS-UBM technique.

2. Experimental details:

2.1 Coating deposition:

The nanoscale multilayer CrN/NbN coatings were deposited in HTC 1000-4/ABS, four target system (Hauzer Techno Coatings, Europe B.V., Venlo, The Netherlands) equipped with two HIPIMS power supplies (Hüttinger Elektronik Sp. z o.o., Warsaw, Poland). The industrial size, computer controlled machine consists of a centrally placed rotating substrate table capable of three fold planetary rotation in a chamber volume of 1 m^3 . The substrates can be suitably biased with the help of a bias power supply. The system comprises of 4 rectangular cathodes, which can be operated in steered CA, UBM or HIPIMS mode. Figure 1(a) shows the schematic cross-sectional view of the machine depicting the substrate holder,

arrangement of the cathodes and the closed magnetic field due to the external electromagnetic coils surrounding the magnets [16].

Figure 1(b) shows the schematic of the coating design. For this study, CrN/NbN coatings were synthesised in a sequence of three steps – pre-treatment, base layer deposition, and bulk coating deposition comprising of nanoscale multilayer structure. The substrates were pretreated with Cr^+ produced in a HIPIMS plasma discharge operating in Ar atmosphere. After etching a base layer of CrN was deposited operating one Cr cathode in HIPIMS mode and one Cr cathode in UBM mode. During the bulk coating deposition two magnetrons furnished with a Nb and a Cr target were operated in HIPIMS mode along with two magnetrons which were operated in a standard UBM mode in a combined N_2 and Ar atmosphere. This process will be referred to as HIPIMS-HIPIMS (H-H).

For comparison of the microstructure, mechanical properties and corrosion performance between coatings, depositions were also carried out by the HIPIMS-UBM (H-U) technique and results have been compared with the previous reported work on the ABS technique [7]. For CrN/NbN deposited by the combined H-U, HIPIMS was used for substrate pre treatment only whereas the coating was deposited by standard UBM technique. The ABS technique (previous work [7]) utilised cathodic arc etching followed by the UBM deposition. Table 1 summarises the process modes operating during the different coating deposition stages. In all the cases Cr^+ etching has been utilised to enhance the adhesion by a low energy ion implantation which takes place during the substrate bombardment. The coatings were deposited on 1 micrometre polished high speed steel and 304L stainless steel substrates which were subjected to three-fold rotation. The deposition temperature was maintained at 400°C whereas the bias voltage (U_b) was maintained at -75 V.

2.2: Plasma diagnostics:

The HIPIMS and conventional dc plasma composition was investigated in a Kurt J Lesker CMS-18 sputtering machine equipped with 3-inch cathodes. An energy-resolved mass spectrometer (Hiden Analytical) was utilised to investigate the relative percentages of reactive gas (Nitrogen), Argon and Cr metal ions in the plasma. All measurements were carried out in a time-averaged manner. More details of the setup are given in Ehasarian et al [17]. The plasma conditions were as close as possible to the ones used in the Hauzer HTC-1000/ABS coater during deposition. The cathodes had identical magnetic field strength, and the discharge was operated at the same current density, total pressure, and Nitrogen partial pressure as the ones used during deposition.

2.3 Coating characterisation:

The coatings were characterised using a number of analytical techniques. Coating thicknesses were measured by ball cratering method using a 30 mm diameter ball using a CSEM CALOWEAR apparatus. Coating adhesion was measured by progressive loading scratch tests conducted on CSEM REVETEST, and the critical load (L_c) of coating failure was observed under optical microscope. Dry sliding wear rates and friction coefficient were measured with a pin on disk apparatus (CSM TRIBOMETER) by sliding a 6 mm Al_2O_3 ball under a load of 5 N at a linear speed of 0.1 ms^{-1} for a total distance of 3769 meters (60000 laps). The Knoop hardness of the coatings was measured with a MITUTOYO microhardness tester using a load of 25 g whereas the Young's modulus was calculated from the loading-unloading curves obtained from a CSM nanoindentation tester. A laser profilometer (UBM

make) was used to profile the wear tracks and to calculate the roughness of the as deposited coating surface.

In order to investigate the effect of the deposition technology on the microstructure of the coatings, Transmission Electron Microscopy (Phillips EM 420) and Scanning Electron Microscopy (FEI NOVA-NANOSEM 200) were used. The bi-layer period was determined by low-angle (2θ , $1-10^\circ$) x-ray diffraction (XRD) in Bragg-Brentano geometry (PHILIPS XPERT). The preferred orientation in the nanoscale multilayer structure was investigated using glancing angle XRD (2θ , $20-100^\circ$).

The effect of deposition technique on the corrosion performance was investigated by potentiodynamic polarisation technique (Princeton Corrosion monitoring apparatus-EG&G Model 263A). The coated SS specimens were polarised from -1000 mV to +1000 mV at a scan rate of 0.5 mVs^{-1} in a 3% NaCl solution aerated for 25 minutes. Prior to being polarised, the specimens were cathodically cleaned at -1500 mV for 150 s. The specimens were masked using bee's wax to expose a desired area of 1 cm^2 to the solution.

3. Results and discussion:

3.1 Plasma characterisation:

The plasma composition in HIPIMS and DC of Cr were compared to estimate the difference between the two technologies.

Plasma composition:

Figure 2a is a mass spectrum of HIPIMS of Cr in a mixed Ar and N₂ atmosphere identical to the one used for deposition of the nanolayer coating. The main ions observed are Cr⁺, N⁺, N₂⁺, and Ar⁺. It is interesting to note that the relative content of Cr⁺ and N⁺ ions is very high with 32 and 11 percent respectively. This signifies a highly ionised metal composition allowing high efficiency of energy transfer to the film. The high content of N⁺ ions indicates a highly reactive plasma process. The energy spectra for all ions are shown in the inset of Figure 2a. A high energy tail is observed particularly in the case of Cr⁺ but also for Ar⁺ and N₂⁺. For Cr ions, 90 % of all particles have energy up to 5 eV.

In comparison, the mass spectrum of conventional dc sputtering of Cr is shown in Figure 2b. In this case the dominating ions are N₂⁺ and Ar⁺. The content of Cr⁺ and N⁺ is strongly depleted (6 % and 5% respectively) which is in contrast to the observations for HIPIMS. Furthermore, the energy spectrum shows that the inherent energy of ions in this case is very low with 90% of ions having energy of < 2eV.

The results from mass spectroscopy indicate that during HIPIMS stage of the deposition, the coatings grow under conditions of highly energetic ion bombardment where metal ions and highly reactive dissociated N⁺ ions comprise a significant fraction of the flux thus contributing to densification of the films with their high mobility. In the dc stage of deposition, the flux comprises mainly of gas ions that contribute their energy indirectly in the case of Ar and deliver half the energy upon dissociation in the case of N₂ [18].

Substrate current:

The operation of HIPIMS during deposition influenced strongly the current to the substrate table. When all four cathodes were operated in DC mode at 8 kW, the total current (average current) to the substrate table was 24 A. When one cathode was operated in HIPIMS mode, it alone provided 30 A of substrate current (peak current). During deposition, cathodes were operated in HIPIMS mode and two in DC mode. The bias current had a constant dc level of 15 A and additional peaks from the HIPIMS pulses of 30 A from each cathode. Despite the high peak currents, the low duty cycles allowed the substrate temperature to be controlled with additional heaters within the intended operation limits of the process.

3.2 Mechanical properties:

The thickness of all the coatings deposited was in the range of 3-5 micrometres depending on the deposition technique. Table 2 shows the characterisation results for the 3 types of coatings deposited. Results indicate that the ABS deposited coatings had a higher hardness ($HK_{0.025} = 3300$) value than the H-H deposited ($HK_{0.025} = 3025$). Although the H-H coating is thinner than the ABS coating, both the coatings have comparable scratch adhesion critical load value. The coatings deposited by H-U technique exhibited hardness in the range of $HK_{0.025} = 2725$ with the highest $L_C = 58$ N for coating adhesion failure.

3.3 Coating microstructure:

The low angle Bragg-Brentano (1° - 10° , 2θ) technique was used to calculate the bi-layer period in the nanoscale multilayer structure. The bi-layer period for the H-H deposited coatings was 4.1 nm whereas for the H-U and the ABS coating it was 2.5 nm and 3.4 nm respectively.

The texture of the coating was investigated by the glancing angle XRD technique (2°). Figure 3 shows the XRD pattern obtained for the two CrN/NbN coatings. Coatings deposited by the H-H technique exhibited a fcc NaCl structure with (200) preferred orientation whereas the H-U deposited coating exhibited a more random orientation. It was reported that with increasing ion bombardment the texture of CrN shows a shift from (111) to (220) preferred orientation [19]. In the present study, EDX analysis of the H-H coatings showed that the ratio of atomic percentage of Cr to Nb was around 2:1. Hence the dominating peak (200) in the H-H coating can be a result of the increased ion bombardment due to HIPIMS plasma and higher percentage of atomic Cr in the coating. Previously deposited multilayer CrN/NbN coatings which were grown on a cathodic arc treated interface [1, 7] with the ABSTM (CA+UBM) technique exhibited a (200) preferred orientation. In this case the UBM deposited (H+U) CrN/NbN coating exhibits dominating (111) and (200) peaks, a change, which could be as a result of the HIPIMS interface between the substrate and the coating which promotes epitaxial growth in the coating.

Coatings deposited by conventional magnetron sputtering can have intercolumnar porosity and less dense structures whereas coatings produced by cathodic arc and the ABS techniques have the additional limitations of droplet formation and shadowing effects which lead to

growth defects and porosity [3-5]. The coating microstructure depends on a number of factors such as the deposition temperature, energy of neutrals controlled by the gas pressure, energy of ions controlled by the substrate bias voltage and the metal ions/ neutral ratio [20,21,]. Coating microstructure density and the quantity of defects (voids) will also depend on the ad-atom mobility on the surface of the substrate. The ad-atom mobility can be increased by suitably biasing the substrate to increase the energy of adatoms and / or by increasing the metal ion flux incident on the substrate surface to increase the proportion of adatoms with high mobility [21]. It has been shown that; with HIPIMS, the metal ion to neutral ratio is much higher and the plasma can contain doubly charged metal ions in contrast to conventional magnetron sputtering and hence can be used to deposit dense coatings [13]. Though plasmas generated by Cathodic Arc (CA) can also be rich in metal ions, the metal droplets deposited can hinder the functional properties of the coating to a large extent [6, 13].

In this study TEM and SEM were used to analyse the microstructure of the deposited CrN/NbN coatings. Figure 4 (a-c) are TEM micrographs for the coatings deposited by the H-H, H-U and the ABS technique respectively showing that a nanoscale multilayer structure was achieved for all the three coatings deposited. As evident from the micrographs, figure 4 (a-c), the nanolayer structure for the coatings deposited by H-H technique was flat, uniform and with sharp interfaces as compared to the other techniques.

At lower magnification, the H-H coatings, figure 5 (a), were dense in structure with no intercolumnar voids; in contrast the H-U coatings figure 5(b) exhibited a number of intercolumnar voids. Due to high degree of ionisation of the metal and the high proportion of highly reactive and mobile nitrogen atomic ions during deposition in the H-H process, the

overall ion-to-neutral ratio is significantly increased and the ad-atom mobility is much higher than in the H-U case. As a result, coatings produced by the H-H technique were found to be denser and had a smoother surface (columns thinner and flatter) as compared to the UBM and ABS technique. This can lead to the nanoscale multilayer structure being uniformly thin and flat with fewer voids.

Laser profiling of the coating surface confirmed that the H-H coatings were significantly smoother with Ra value of 0.061 μm than the H-U and the ABS coating with Ra values of 0.078 μm and 0.072 μm respectively (table 3). The smoothness of the surface can be attributed to the dense and uniform microstructures of the coating and the absence of droplets deposited during CA etching which protrude from the coating surface. Figure 6 shows the top of the H-H and H-U coatings observed in cross section by TEM and in plane-view by SEM. The grain column tops in the H-H coatings, figure 6(a), were found considerably flatter and smaller as compared to the dome shaped broad grain columns in the H-U coating, figure 6 (b). The difference in column topography was confirmed in the high resolution SEM plane view figures 6 (c-d). In the H-U case the columnar boundaries were well defined. These boundaries can represent the compaction factor of the growing columns. The wider and more prominent the grain boundary, the higher is the possibility of the space (void) between the grain columns. More dome shaped columns have a higher probability of intercolumnar void formation due to shadowing effect. In contrast, in the H-H case some column boundaries are obscured indicating a strong intercolumnar connection and high intercolumnar density. The beneficial effect of the HIPIMS plasma is evident in the H-H coatings even though only two magnetrons were operating in the HIPIMS mode.

3.4 Dry sliding wear: Friction coefficient and Wear coefficient:

Table 3 compares the roughness, friction coefficient and the sliding wear rates recorded for the deposited CrN/NbN coatings.

The dry sliding wear coefficient of the H-H coating was factor 1.6 smaller as compared to the H-U whereas it was smaller by a factor of 1.3 as compared to the ABS coatings. For both the coatings, H-H and H-U, wear of the 6 mm Al₂O₃ ball counterpart was negligible.

Lower wear rates for the multilayer coatings as compared to the monolithic coatings, can be attributed to the unique layer by layer material removal mechanism [22]. The interfaces in the multilayer coatings confine crack propagation by deflecting it at the interface [23]. Coating structures with uniform multilayer structure and sharp interfaces hence can lead to lower wear rates; as evident in the H-H coatings. Figure 7 shows the SEM images of the wear track on the H-H coating. The wear track in general appeared to be smooth with faint grooves associated with 2 body and 3 body ploughing action of the counterpart and the wear debris, figure 7 (a). Even at higher magnification, figure 7 (b) wear track appeared smooth with very small size (few hundred nanometres in width) grooves suggesting material removal (wear debris formation) at nanoscale levels or in other words layer by layer removal of the coating. Thus the results observed were consistent with the literature [15, 22].

The improved wear rates of the H-H coating over H-U and ABS coatings can be attributed to the lower number of intercolumnar voids in the H-H case. The strong contact between columns means that columns support each other and the overall structure is more resistant against tangential loads as seen in sliding wear. This hinders plastic deformation and cracking during wear and reduces the removal rate of particles from the coating [7].

Figure 8 is a plot of the coefficient of friction against sliding distance for the H-H and H-U coatings.

As observed in figure 8a, friction coefficient of the H-H coating reached a value around 0.40 after the initial 'run-in' period followed by a steady state value around 0.32 ± 0.02 (averaged over sliding distance from 1000 to 2000 m). It increased slowly to values around 0.35 until 2500 m, increasing as high as 0.73 for a very brief period before ending at a value of 0.41 at the total sliding distance of 3769 m (60000 laps). For the H-U coatings, figure 8b, the friction coefficient behaviour was unstable and fluctuated between 0.84 and 1.02 until 2000 m. For sliding distances between 2000 and 2500 m the friction coefficient progressively decreased to reach the minimum of 0.28 and increased again to finish at 0.78, at the end of 60000 laps. The steady state friction coefficient of the H-H coating observed is significantly lower as compared to most nitride coatings reported in literature (considering the extreme test duration of 60,000 laps) [24-27] which is a beneficial effect of the denser microstructure.

3.5 Corrosion performance:

Previous work showed that the corrosion performance of the ABS deposited 5 micrometres thick nanoscale multilayered CrN/NbN coating was superior to 20 micrometres hard chrome coatings [1]. However the defects in the ABS and UBM grown coating (growth defects, porosity and intercolumnar voids) can limit their corrosion performance. The growth defects and the intercolumnar voids can provide solution path galvanic corrosion whereby the corrosive solution reaches the substrate through these defects [10]. An effective way of increasing the corrosion resistance is to deposit coatings with electrochemically noble metals having very dense structures and with minimum or no growth defects. Thus HIPIMS

technique provides a unique means of depositing dense structures and thus effective corrosion resistant coatings.

Figure 9 shows the potentiodynamic polarisation curves for the H-H, H-U, ABS coated and uncoated stainless steel. The results indicate superior corrosion performance for the H-H coatings as compared to the H-U and the ABS coatings.

The results in the past have shown that substrate pre-treatment (etching) with HIPIMS can compositionally modify the interface between substrate and the coating thereby improving the corrosion resistance of the coating [14]. In agreement with those results, the H-U coating exhibited superior pitting resistance in the potential range + 600 mV to + 820 mV as compared to the ABS coating. The pitting resistance of the ABS coating was only evident in the potential range between + 400 mV and + 600 mV where the coating shows passivation. However the corrosion current increased with the potential without any further evidence of passivation (with exception in between + 780 mV and + 800 mV).

As observed in the polarisation curves (figure 9), E_{corr} value of H-H coating ($E_{\text{corr}} = + 400$ mV) was more noble as compared to the ABS ($E_{\text{corr}} = + 334$ mV) and the H-U coatings ($E_{\text{corr}} = + 332$ mV). Pitting resistance of the H-H coatings was more evident in the potential range + 400 mV to + 500 mV and + 900 mV to + 1000 mV where the coated specimen indicates passivation. For the rest of the anodic potential range the results suggested dissolution of the coating or galvanic corrosion between the substrate and / or the layers of the coating [28]. However the H-H coating had lower corrosion current densities (up to 2 magnitudes lower at all anodic potentials) as compared to H-U and the ABS coating for all the anodic potentials suggesting superior corrosion performance. It is noteworthy that, though the H-H coatings

were the thinnest of the three, they outclass the corrosion performance of the H-U and the ABS coating.

In general, the coatings deposited by the H-H technique demonstrated better corrosion resistance as compared to the H-U and the ABS coating. These results indicate superior coating structures; in terms of reduced growth defects and dense microstructures, as the involvement of HIPIMS increases in the deposition stages.

4 Conclusions:

Nanoscale multilayer CrN/NbN PVD coatings were successfully deposited in an industrial sized Hauzer HTC-1000-4/ABS PVD coater with the HIPIMS, UBM and the ABS techniques. The coatings had a bi-layer thickness in the range of 2.5 - 4.2 nm. TEM results indicate that the coatings produced by the HIPIMS technique have a highly uniform dense and well defined microstructure with flat nanolayers and sharp interfaces.

The superiority of the HIPIMS coating was further evident with its corrosion performance surpassing the coatings employing CA, HIPIMS etching and UBM deposition. The E_{corr} value and the pitting resistance of the H-H coating were superior to that of the H-U and the ABS coating. The corrosion current density of the H-H coating was lower than the H-U and the ABS coating at all potentials. In general, the results indicate that use of HIPIMS technique produces better coatings and that the performance enhances as the role of HIPIMS increases in the deposition steps.

References:

- [1]. W.-D. Munz, L.A. Donohue, P. Eh. Hovsepian, Surface and Coatings Technology, 125 (2000) 269-277.
- [2]. P. E. Hovsepian, D.B. Lewis, W.-D. Munz, A. Rouzaud, P. Juliet, Surface and Coatings Technology 116-119 (1999) 727-734.
- [3]. P. Eh. Hovsepian, D.B. Lewis, W.-D. Munz, S.B. Lyon, M. Tomlinson, Surface and Coatings Technology 120-121 (1999) 535-541.
- [4]. E. Bemporad, C. Pecchio, S. De Rossi, F. Carassiti, Surface and Coatings Technology 188-189 (2004) 319-330.
- [5]. D.C. Cameron, R. Aimo, Z.H. Wang, K.A. Pischow, Surface and Coatings Technology 142-144 (2001) 567-572.
- [6]. R.J. Rodriguez, J.A. Garcia, A. Medrano, M. Rico, R. Sanchez, R. Martinez, C. Labrugere, M. Lahaye, A. Guette, Vacuum 67 (2002) 559-566.
- [7]. A.P. Ehasarian, P. Eh. Hovsepain, L. Hultman, U. Helmersson, Thin Solid Films 457 (2004) 270-277.
- [8]. I. Petrov, P. Losbichler, D. Bergstrom, J.E. Greene, W.-D. Münz, T. Hurkmans and T. Trinh, Thin Solid Films, 302, Issues 1-2, 20 (1997) 179-192.
- [9]. H.W. Wang, M.M. Stack, S.B. Lyon, P. Hovsepian, W.-D. Munz, Surface and Coatings Technology 135 (2000) 82-90.
- [10]. H.W. Wang, M.M. Stack, S.B. Lyon, P. Hovsepian, W.-D. Munz, Surface and Coatings Technology 126 (2000) 279-287.

- [11]. Y.P. Purandare, M.M. Stack and P.Eh. Hovsepian, Surface and Coatings Technology 201, 1-2, (2006) 361-370.
- [12]. M. Fenker, M. Balzer, H. Kappl, Thin Solid Films, 515 (2006) 27-32.
- [13]. A.P. Ehasarian, W.-D. Munz, L. Hultman, U. Helmersson, I. Petrov, Surface and Coatings Technology 163-164 (2003) 267-272.
- [14]. C. Reinhard, A.P. Ehasarian, P. Eh. Hovsepian, Thin Solid Films 515 (2007) 3685-3692.
- [15]. A. P. Ehasarian, A. Anders, I. Petrov, J. Vac. Sci. Technol. A 25(3), 2007.
- [16]. W.-D. Munz, F. J .M. Hauzer, D. Schulze and B. Buil, Surface and Coatings Technology 49 (1991) 161-167.
- [17]. A.P. Ehasarian, Y.A. Gonzalvo, T.D. Whitmore, Plasma Process. Polym. 2007, 4, S309-S313.
- [18]. Brian Chapman, Glow Discharge Processes, Sputtering and Plasma Etching, John Wiley & Sons, -Interscience Publication, 1980.
- [19]. J.A. Thornton, J.Vac. Sci Technol., 11 (1974) 666.
- [20]. T. Hurkmans, D. B. Lewis, H. Paritong, J. S. Brooks, W.D. Munz, Surface and Coatings Technology 114 (1999) 52 -59.
- [21]. I Petrov, A. Meyers, J.E. Greene and J.R. Abelson, J.Vac. Sci. Technol.A 12, 2846 (1994).
- [22]. W.-D. Munz, D.B. Lewis, P. Eh. Hovsepian, C. Schonjahn, A. Ehasarian and I. J. Smith, Surface Engineering 2001 Vol. 17 No.1 15-27.
- [23]. H. Holleck and V. Schier, Surface and Coatings Technology 76-77 (1995) 328-336.

- [24]. E.J. Bienk, H. Reitz, N.J. Mikkelsen, Surface and Coatings Technology 76-77 (1995) 475-480.
- [25]. U. Wiklund, O. Wanstrand, M. Larsson, s. Hogmark, Wear 236 (1999) 88-95.
- [26]. J.D. Bressan, R. Hesse, E.M. Silva Jr., Wear 250 (2001) 561-568.
- [27]. P.H. Mayrhofer, P. Eh. Hovsepian, C. Mitterer, W.-D. Munz, Surface and Coatings Technology 177-178 (2004) 341-347.
- [28]. M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, NACE publications, Houston, USA.

Figure captions

Figure 1: Schematic diagrams: (a) arrangement of the substrate holder, cathodes and the magnets in an HTC 1000-4/ABS PVD coater [17] (b) CrN/NbN coating layer scheme [1].

Figure 2: Mass and energy spectra of a) HIPIMS of Cr and b) conventional dc sputtering of Cr in Ar and N₂ atmosphere as used to deposit the CrN/NbN nanolayer coating.

Figure 3: X-ray diffraction patterns of the CrN/NbN coating deposited by the H-H and the H-U technique.

Figure 4: TEM micrographs of the nanoscale multilayer structure evident for the CrN/NbN coatings deposited by: (a) H-H technique (b) H-U technique (c) ABS technique.

Figure 5: TEM micrographs showing microstructure details: (a) defect free H-H coating (b) H-U coating evident with intercolumnar voids (highlighted with white markers).

Figure 6: Microstructure of the coatings showing the grain column topography: TEM cross sectional micrographs showing the grain columns tops of the (a) H-H and the (b) H-U coating. SEM plan view micrographs for the (c) H-H and the (d) H-U coatings.

Figure 7: SEM image of the wear track of the H-H coating (a) lower magnification image of the wear track in general. (b) Higher magnification image of the selected area of the wear track shown in the bracket in figure a.

Figure 8: Graph of friction coefficient against sliding distance under dry sliding conditions and Al_2O_3 counterpart: (a) H-H coatings (b) H-U coatings.

Figure 9: Potentiodynamic polarisation curves for the H-H, H-U, ABS coating and uncoated SS polarised from -1000 to + 1000 mV in a 3% NaCl solution aerated for 25 minutes.

Table I: Process scheme of different techniques used to deposit nanoscale multilayered CrN/NbN PVD coatings.

Process	Deposition step	Cathode 1 - Nb	Cathode 2 - Nb	Cathode 3 - Cr	Cathode 4 - Cr
HIPIMS-HIPIMS (H-H)	Etching			<i>HIPIMS</i>	
	Base layer			<i>HIPIMS</i>	UBM
	Coating	<i>HIPIMS</i>	UBM	<i>HIPIMS</i>	UBM
HIPIMS-UBM (H-U)	Etching			<i>HIPIMS</i>	
	Base layer			UBM	UBM
	Coating	UBM	UBM	UBM	UBM
ABS	Etching			<i>CA</i>	
	Base layer			UBM	UBM
	Coating	UBM	UBM	UBM	UBM

Table II: Characterisation results of nanoscale multilayer CrN/NbN PVD coatings deposited by three techniques.

Coating	Thickness (μm)	Bi-layer thickness (nm)	Hardness HK (25g)	Scratch Adhesion (L_C) (N)	Young's Modulus (GPa)
H-H	2.9	4.1	3025	44	412
H-U	4.2	2.5	2725	58	415
ABS	3.6	3.4	3300	45	423

Table III: Comparative values of surface roughness, friction coefficient and sliding wear coefficient of CrN/NbN coatings produced by H-H, H-U and the ABS techniques.

Coating	Roughness, Ra (μm)	Friction coefficient, μ	Sliding wear coefficient ($\text{m}^3\text{N}^{-1}\cdot\text{m}^1$)
H-H	0.061	0.32	1.8×10^{-15}
H-U	0.078	0.46	3.0×10^{-15}
ABS	0.072	0.63	2.2×10^{-15}